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REFINEMENT OF THE WILLIAMS-LANDEL-
FERRY EQUATION

D. S. Sanditov, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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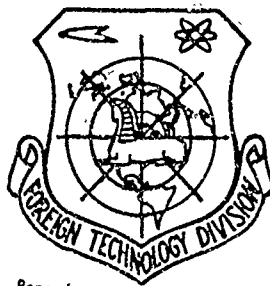
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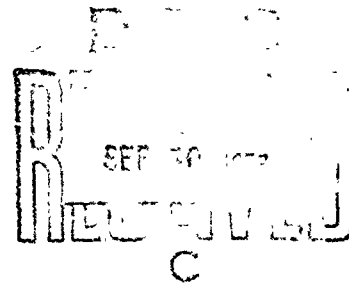
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by

D. S. Sanditov, G. M. Bartenev



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By: D. S. Sanditov, G. M. Bartenev

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

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FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH
DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	sin ⁻¹
arc cos	cos ⁻¹
arc tg	tan ⁻¹
arc ctg	cot ⁻¹
arc sec	sec ⁻¹
arc cosec	csc ⁻¹
arc sh	sinh ⁻¹
arc ch	cosh ⁻¹
arc th	tanh ⁻¹
arc cth	coth ⁻¹
arc sch	sech ⁻¹
arc csch	csch ⁻¹
<hr/>	
rot	curl
lg	log

REFINEMENT OF THE WILLIAMS-LANDEL-FERRY EQUATION

D. S. Sandimov and G. M. Bartenev

The equivalence of the influence of temperature and time on the relaxation properties of polymers was first discovered by Kobeko, Aleksandrov, and Lazurkin [1, 2], and then confirmed by vast experimental data in the works by Linderman, Tobolsky, Ferry, et al. [3, 4].

In polymers, physical relaxation involves two basic processes: 1) orientation and shifting of the free segments of the chain molecules, occurring very rapidly, with relaxation times of 10^{-6} - 10^{-4} s at 20° ; 2) rearrangement of the elements of the supermolecular structure, occurring slowly, with relaxation times within the limits 10 - 10^4 s. In particular, viscous flow of linear polymers involves this second process [5, 6].

These two processes pertain, respectively, to the rapid and slow stages of physical relaxation. The process of the slow relaxation stage is found in the highly-elastic state, and can be approximately described by a discrete relaxation-time spectrum [5]. The process of the rapid stage of physical relaxation, playing the basic role in the glass transition of polymers, can be quite accurately described by the averaged relaxation time along [2, 4].

Table. Values of the constants of equations (1) and (5), characterizing the temperature dependence $a_T(T)$ for various polymer systems.

Amorphous substance	$T_c, ^\circ K$	a_1	a_2, deg	$a_0 = \left(1 - \frac{a_2}{T_c}\right)$
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Organic polymers [4]

Polyisobutylene	202	38.1	104.4	0.50
Natural rubber	204	38.5	53.6	0.82
Polyhexane-1	218	51.1	20.2	0.90
Polyurethane	238	35.6	32.6	0.86
Polymethyl acrylate	276	41.6	45.0	0.84
Polyvinyl chloride-acetate	296	40.1	40.4	0.86
Polyvinyl acetate	305	35.9	46.8	0.85

Inorganic polymers and glass [8]

Vitreous boric oxide	533	42.6	246	0.54
Lead silicate glass	713	32.2	280	0.61
Alkali-silicate glass	783	36.1	284	0.64
Alkali-silicate glass No. 1	788	30.0	260	0.67
Alkali-silicate glass No. 10	828	36.8	320	0.61

Ferry et al. [4] showed that the temperature dependence of the mechanical and electrical properties of amorphous polymers (and also low-molecular amorphous substances) above the glass-transition temperature T_c , approximately in the range $T_c + 100^\circ$, can be described by one empirical function $a_T(T)$, which is the ratio of the rapid stage of physical relaxation at temperature T to a certain reduction temperature T_0 : $a_T = \tau(T)/\tau(T_0)$. As the reduction temperature we usually select T_c , which is the characteristic temperature of amorphous substances.

Since the temperature dependence of the viscoelastic properties can be represented by the unique function $a_T(T)$, it

is naturally very important to carefully study the form of this function and its significance. At present, the so-called Williams-Landel-Ferry equation [4] is widely used to calculate a_T :

$$\ln a_T = -a_1 \frac{T - T_c}{T - T_c + a_2}, \quad (1)$$

where the dimensionless coefficient $a_1 \approx 40$ is a practically universal constant for all amorphous substances (Fig. 1). Constant a_2 has the dimensions of temperature, and initially it was also considered to be universal and equal to 50° . However, this value is valid primarily for a class of substances for which $T_c \approx 250-300^\circ\text{K}$ (see the table). For inorganic glass ($T_c \approx 600-800^\circ\text{K}$), which recently has been examined as polymer systems [7], the values of $a_2 \approx 300^\circ$ [8].

Thus, the value of a_2 depends on the nature of the substance. In addition, equation (1) does not take into consideration the dependence of T_c on the rate of cooling or heating $q = dT/dt$ [1, 7]. In this connection, equation (1) is not universal, although it is frequently designated as such.

The physical significance of equation (1) has been discussed in many works [4]. In particular, we recently showed [9-11] that the constants

$$a_1 = U_c / kT_c \quad (2)$$

$$a_2 = (kT_c / E) T_c \quad (3)$$

where U_c is the activation energy for transfer of a unit (atom, segment) from one equilibrium position to another at T_c ; E is the energy of local disintegration or, in other words, the energy of formation of microcavities on the order of atomic or

segmental dimensions at T_c . It was assumed that the fluctuational formation and disappearance of the microcavities in amorphous polymers above T_c can be associated with the change in conformation (convolution or evolution) of polymer chains due to internal rotation, and also rotation of side chains about the carbon chain. The value of E practically coincides with the potential barrier of hindered internal rotation in polymers (1-4 kcal/mole, and was proportional to the glass-transition temperature [11, 12]

$$E \approx 3kT_c \quad (4)$$

This approximate equality is valid for all studied noncrystalline solids (Fig. 2).

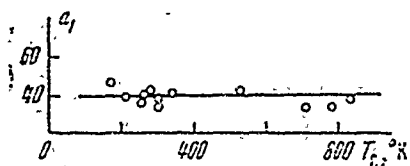


Fig. 1. Correlation between constant a_1 of equation (1) and T_c for organic and inorganic polymers (graph constructed per data by Ferry [4] and Bestul [8]).

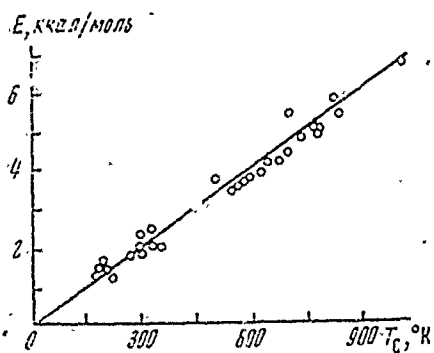


Fig. 2. Dependence of energy of microdisintegration on T_c for various amorphous substances [11, 12].
Designations: ккал/моль =
= kcal/mole.

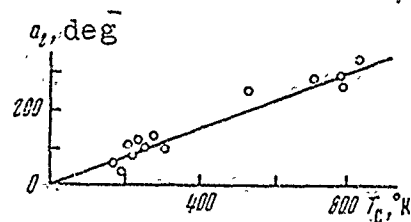


Fig. 3. Dependence of constant a_2 of equation (1) on T_c for various polymer systems.

Since $kT_c/E \approx \text{const}$ according to relationship (4), dependence (3) of coefficient a_2 on T_c should be linear. Actually, the plot, within limits of experiment error, is a straight line with a slope, as was to be expected, approximately equal to (Fig. 3)

$$a_2/T_c \approx 0,32$$

In this regard we easily see that equation (1) can be rewritten in the form [11]

$$\ln a_r = -a_1 \frac{T - T_c}{T - T_c a_0}, \quad (5)$$

where the coefficient

$$a_0 = \left(1 - \frac{a_2}{T_c}\right) = \left(1 - \frac{kT_c}{E}\right) \approx 0,68, \quad (6)$$

unlike a_2 , is dimensionless and practically independent of the type of polymer (table).

Thus we have obtained a more universal form of equation (1). However, in equation (5), just as in (1), T_c cannot be considered a constant since it depends on the rate of change in temperature per the familiar Bartenev-Luk'yanov equation [13, 14].

$$\frac{1}{T_c} = C_1(1 - C \lg q), \quad (7)$$

where $C \approx 0.03$ is a universal constant, while C_1 varies from $3 \cdot 10^{-3}$ to 10^{-3} deg^{-1} for various amorphous substances. This equation, proposed by one of the authors [13], is valid for a broad range of organic and inorganic polymers [7]. The interconnection between equations (1) and (7) has been studied in prior works [9-11]; in particular, it was shown [9] that $C \approx kT_c/U_c \approx 1/a_1$.

Consequently, we must show at what cooling rate T_c was determined, or reduce all values of T_c to some single standard value. According to Bartenev and Luk'yanov [14], as the "standard" glass-transition temperature T_c^{CT} we can arbitrarily use that temperature for which relaxation time $\tau = 10^2$ s and the viscosity is 10^{13} poise. The glass-transition temperature determined by dilatometry at a cooling rate of 3 deg/min (0.05 deg/s) approximately corresponds to the standard temperature. Considering that when $q = q^{CT} = 3$ deg/min in equation (7) constant C_1 is $\sim 1/1.04 \cdot T_c$, it is easy to obtain a formula for the transition from T_c , measured at an arbitrary cooling rate, to T_c^{CT} , measured at the standard rate $q^{CT} = 0.05$ deg/min:

$$T_c = T_c^{CT} \left(\frac{1.04}{1 - 0.03 \lg q} \right) \quad (8)$$

From this we see that a change in cooling rate by one order of magnitude leads to a change in glass-transition temperature $\Delta T_c = 0.03 T_c$. For example, when $T_c = 500^\circ K$, the value $\Delta T_c = 23^\circ$, i.e., the error will considerably exceed the usual experiment error.

Considering dependence (8), equation (5) can be rewritten in stricter form:

$$\ln a_T = -a_1 \frac{T - T_c^{CT} \left(\frac{1.04}{1 - 0.03 \lg q} \right)}{T - T_c^{CT} a_0 \left(\frac{1.04}{1 - 0.03 \lg q} \right)} \quad (9)$$

Let us note that in the dilatometry of polymers and glass, in many countries a cooling or heating rate close to the standard 3 deg/min is used; therefore, literature data for the glass-transition temperature actually refer to standard temperatures. Consequently, in practice we can use equation (5) in place of (9), considering that $T_c = T_c^{CT}$ in it.

As shown recently by Slonimskiy, Askadskiy, and Kitaygorodskiy [15], the packing coefficient for molecules of amorphous polymers having the most diverse structures is equal to ~ 0.68 , i.e., it coincides with the value of the constant $a_0 = (1 - kT_c/E)$ in equation (5). The packing coefficient is the ratio of the natural volume of the atoms comprising the molecules to the volume of the substance, defined per its density.

Conclusions

We propose a refinement of the Williams-Landel-Ferry equation for the temperature dependence of the relaxation time during the rapid stage of physical relaxation of polymers above the glass-transition temperature T_c . In this equation we have considered the dependence of T_c on the cooling rate; in place of coefficient a_2 , having the dimension of temperature and a function of the type of polymer, we have introduced a dimensionless, practically universal constant $a_0 = (1 - a_2/T_c) \approx 0.68$.

Moscow State Pedagogical Institute
im. V. I. Lenin

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Buryat State Pedagogical Institute
im. D. Bandarov

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